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Intramolecular co-operative hydrogen bond in calix[n]arenes (n = 4, 6, 8) bearing bulky substituents

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Abstract

Based on the Fourier transform IR spectroscopy together with the published NMR and X-ray data, it was shown that cyclic co-operative intramolecular hydrogen bond in calix[n]arene (n = 4, 6, 8) molecules is mainly responsible for their conformational state irrespective of the presence or absence of bulky substituents at the upper rim of the molecules. In accordance with the size of a macrocycle (n = 4, 6, 8), the stable conformation, secured by such a hydrogen bond, constitutes a cone, a pinched cone, and a pleated loop, respectively. The new, potentially competing system of hydrogen bonds in calix[6]arenes with 3-carboxymethyl-1-adamantyl substituents does not affect the conformational state of the macrocycle and its H-bonding. Six carboxy groups at the upper rim form in pairs three cyclic dimers, which does not disturb the hydrogen bonds of the hydroxy groups and the conformation of the macrocycle. In addition, the cavity of the molecule is considerably enlarged. The removal or rearrangement of the guest molecules in the solid calixarene by heating up to 180 °C only slightly affects the conformational state of macrocycles bearing bulky substituents, whereas in calixarenes devoid of such substituents, the similar procedure leads to somewhat of a distortion of the macrocycles (judging from the IR spectral indications of hydrogen bonding).

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Keywords

Calix[n]arenes, Conformers, Fourier transform IR spectroscopy, Hydrogen bond